

Quantum Mechanical and Semi-Classical Theory of Relaxation

Valerij G. Kiselev, PhD

Medical Physics, Department of Diagnostic Radiology, University Hospital Freiburg. Hugstettersrt. 55,
D-79106 Freiburg, Germany

1 Introduction

The goal of this lecture is to explain the mechanisms of relaxation caused by the thermal motion of molecules. The text consists of two main parts. The physics of relaxation is discussed in a simple way in section 2. This yields a qualitative understanding of experimental facts. The necessary results from quantum mechanics are to be believed, as they are used without a proof. This is thought for the reader who does not need a guided tour in the laboratory of quantum mechanics. The prerequisites for the understanding of this part are the very basic notions of quantum mechanics, statistical physics and Fourier transformation. In the rest of the text, section 3, a more involved analysis is presented that verifies the assumption made and introduces a method that enables a quantitative analysis of relaxation. The reader is expected to possess basic knowledge in linear algebra, differentiation and integration and be acquainted with the notion of correlation functions. The described way of presentation is in line with that by Goldman [1, chapter 9] the book by whom is the main reference in this lecture.

2 Qualitative Description of Relaxation

2.1 Description of Spin 1/2

In this lecture, we focus on spins of atomic nuclei of molecules in the liquid state. The spin of such particles can be manipulated by applying magnetic fields. We consider only particles with the spin $s = 1/2$ such as protons in molecules of water and other substances.

A spin can be thought of as the angular momentum of a rotating elementary particle treated as a massive body. The angular momentum is an arbitrary vector in classical physics. In quantum mechanics its length is quantized, that is it can take only discrete values. The direction of such a vector is arbitrary being described by two angles as illustrated in Fig. 1. The presence of unexplained restriction reflects the inconsistency of the classical interpretation of spin.

A consistent description of individual spins can be achieved only in terms of quantum mechanics. A spin is described by a wave function which takes the form of a spinor with only two independent parameters:

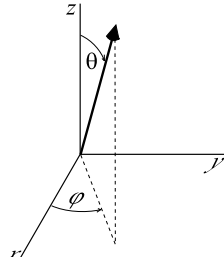
$$\psi = \begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} \cos \theta \\ \sin \theta e^{i\varphi} \end{pmatrix} \quad (1)$$


Fig. 1

Here the first form of ψ represents a generic spinor with two complex-valued components. The components, u and v , are the probability amplitudes of finding the particle in the states with the spin projection on the z -axis $+\hbar/2$ and $-\hbar/2$ respectively.

The z-axis is conventionally selected to be parallel to the external magnetic field. In such a field there are two states with definite energy that are described by the spinors

$$\psi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \psi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (2)$$

These states are commonly referred to as "spin up" and "spin down". An arbitrary spin in Eq. (1) is a quantum superposition of these basis states with the coefficients u and v . The energy of these states is $E_{\pm} = \mp \hbar \omega_0 / 2$, where $\omega_0 = \gamma B_0$ is the Larmor frequency and $\gamma = 2.67522 \times 10^8 \text{ s}^{-1} \text{ T}^{-1}$ [2]. Note that the subscript " \pm " refers to the orientation of spin. The energy of spin in the state ψ_- is higher than in the state ψ_+ .

According to this meaning, the common phase of the spinor is irrelevant, and the probability of any measurement result, which is $|u|^2 + |v|^2$, must equal unity. The four real parameters of the two complex numbers are thus reduced to two. The meaning of those is illustrated in the second form in Eq. (1). The spinor is parametrised with two angles, θ and φ that define the orientation of the expectation value of the spin. This expectation value is a vector of fixed length $[s(s+1)\hbar^2]^{1/2} = 3^{1/2}\hbar/2$. It is the classical angular momentum mentioned above. This vector is obtainable in a large number of measurements with particles prepared in the state described by the spinor in Eq. (1). This can be fulfilled in a single measurement of a large number of spins in the same state, an experiment similar to the signal acquisition in NMR.

2.2 Two Kinds of Relaxation

An isolated spin is an extremely simple system. In real samples, the nuclear spins are never isolated being subjected to interactions with each other and the surrounding medium. The latter is typically in thermal equilibrium with a definite temperature T . As a part of the large system the nuclear spins have the same equilibrium temperature which implies a definite ratio between the probabilities of finding a spin in one of the two quantum levels: $|u|^2/|v|^2 = e^{-\hbar\omega/kT}$, where $k = 1.380658 \times 10^{-23} \text{ JK}^{-1}$ is the Boltzmann constant.

Our first question is how fast this equilibrium is reached after being disturbed, for example, by a radio frequency pulse. The process of changing the populations of the two energy levels toward the equilibrium is called the *longitudinal relaxation*. The standard notation for its time constant is T_1 .

Another kind of relaxation takes place if the spins acquire a magnetization in a direction transverse to the main magnetic field, that is when $\theta \neq 0, \pi$ in Eq. (1). Such a magnetization can be created with a radio frequency pulse. Its component, which is transverse to the main field, precesses with the Larmor frequency. Right after the excitation, all spins have the same precession phase, which is the angle φ in Eq. (1). This phase coherence degrades with time resulting in a decrease in the measured signal which is proportional to the vector sum of contributions of individual spins. This process of signal attenuation is called the *transverse relaxation*. The standard notation for its time constant is T_2 . Our second question is how fast the transverse magnetization decays. We focus here on the microscopic mechanisms of transverse relaxation that are effective on the molecular scale assuming a perfectly homogeneous main magnetic field. The effect of local heterogeneity of this field, which is an issue in living tissue, is considered in the next lecture [3].

2.3 Qualitative Analysis of Relaxation

We proceed now with a qualitative application-oriented analysis of the relaxation. It is based on the resonance character of transitions in quantum mechanical systems as presented in the next paragraph. Basis experimental facts are discussed in the next sections.

The interaction between a spin and the environment is mediated by random magnetic fields arising due to the thermal motion of molecules. There are three main processes contributing in such fields. The first is the thermal motion of electric charges formed by different charge densities of electrons and nuclei in molecules. The second is the effect of nuclear magnetic moments and the third is the effect of electron magnetic moments. The first effect is weaker than the second. The magnetic dipole-dipole interaction is the main source of the relaxation in diamagnetic substances.

The electron magnetic moment is three orders in magnitude larger than that of nuclear spins, but its effect is compensated by the opposite orientation of electron spins in the pairs of coupled electrons. Uncoupled electrons when present have a strong effect on the relaxation of nuclear spins. Such electrons are present in free radicals and on inner electron shells in some heavy elements such as gadolinium. A medium with uncoupled electrons is paramagnetic.

We will characterize the very complex random field with only two parameters: the averaged strength of the field at the position of a spin and the characteristic time constant of variations of this field. The field strength is characterized by the shift in the Larmor frequency of the proton, Ω . The time constant is called the correlation time, τ . The aim of this section is to estimate the dependence of the relaxation rates on these parameters.

The random magnetic fields cause transitions between the two basic states of a given spin which is the mechanism of relaxation. According to quantum mechanics, the transition between different states is a resonance process. Its rate is proportional to the spectral density of the random field at the frequency, ω , that corresponds to the energy difference, ΔE , between the initial and final states, $\omega = \Delta E/\hbar$.

For the longitudinal relaxation, these states are ψ_{\pm} as defined in Eq. (2). The transition between them can be thought of as a change of angle θ in Eq. (1). A more accurate description is given below in section 3. The energy difference between these basis states is $\Delta E = \hbar\omega_0$ and the corresponding frequency is the Larmor frequency $\Delta E/\hbar = \omega_0$.

For the transverse relaxation, the transitions take place between the states that have different φ in Eq. (1) and the same θ . These states are quantum superpositions of the basis states in Eq. (2). For example, the state with the polarization along the x-axis is described by Eq. (1) with $\theta = \pi/2$ and $\varphi = 0$ and the state with the polarization along the y-direction has $\theta = \pi/2$ and $\varphi = \pi/2$. The energy difference between them is zero.

Consider now the spectral density of the perturbation. It is typically a decreasing function of frequency as illustrated in Fig. 2. The width of the peak is given by the inverse correlation time. The integral of the spectral density over all frequencies is the standard deviation of the instant field. As such, it is independent on the correlation time. That is why the magnitude of the peak at $\omega = 0$ is proportional to τ (Fig. 2).

We thus conclude that the transverse relaxation rate, $R_2 = 1/T_2$, which is defined by the spectral density at $\omega = 0$, should be proportional to the correlation time as illustrated with the blue line in Fig. 3. The longitudinal relaxation shows a more complex behavior. The spectral density at the Larmor frequency is small for small and large τ (Fig. 2). It has a maximum at $\omega_0\tau \sim 1$. The longitudinal relaxation is proportional to this spectral density as illustrated in Fig. 3. The longitudinal relaxation rate, $R_1 = 1/T_1$, reaches a maximum for an intermediate correlation time such that $\omega_0\tau \sim 1$. Taking the inverse of the relaxation rates, we come to Fig. 4 which illustrates schematically the correlation time dependence of T_1 and T_2 .

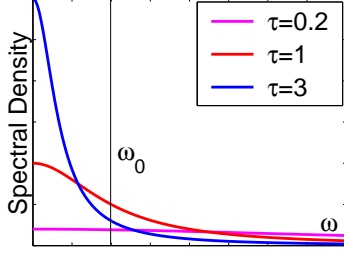


Fig. 2

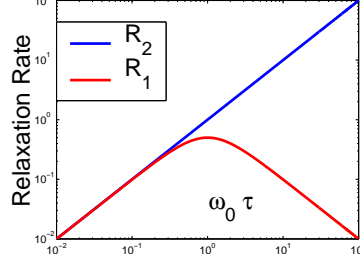


Fig. 3

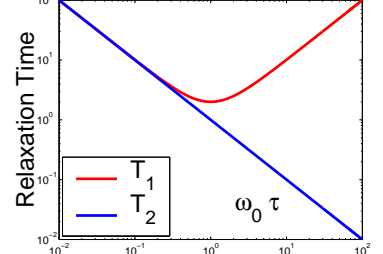


Fig. 4

Let discuss the dependence of the relaxation on the strength of the dipole-dipole interaction, Ω . This value is typically much smaller than the Larmor frequency. Its effect is just a power series in Ω with only low order terms relevant. The term proportional to Ω turns to zero being proportional to the averaged first power of the random magnetic field. The relaxation effect comes from the second-order term which has a nonzero mean during the correlation time. Consequently, the relaxation rate should be proportional to Ω^2 .

2.4 A Brief Discussion of Experimental Facts

The dependences represented in the above figures form a basis for analysing the relaxation process in liquids. Consider first pure water. The correlation time τ is defined by the molecular motion. The rate of molecular tumbling can be estimated by equating the kinetic energy of protons, $m_p v^2/2$ to the thermal energy $kT/2$. Using the constants $m_p = 1.7 \times 10^{-27}$ kg and $k = 1.4 \times 10^{-23}$ J/K, we obtain $v = 4 \times 10^{-2}$ m/s. A particle with such a velocity traverses the characteristic atomic size about 10^{-10} m in $\tau = 3 \times 10^{-13}$ s, which is our estimate for the correlation time. A similar estimate for the translation motion gives a few times longer time, since τ is proportional to the square root of m , which should be replaced with the mass of the whole molecule. The cyclic Larmor frequency at 1.5 T is $\omega_0 = 4 \times 10^8$ s $^{-1}$. Thus, the relaxation in water occurs deeply in the regime of short correlation times, $\omega_0 \tau = 10^{-4} \ll 1$. Accordingly, $T_1 \approx T_2$ and both relaxation times are very long (longer than one second). Note that T_2 in tissue is shortened significantly by microscopic heterogeneity of the magnetic field and other effects [3].

Large molecules move slowly. That is why protons of lipids experience random magnetic fields with a longer correlation time. This explains a shorter T_1 in fat tissue, the fact commonly used for the fat suppression with the inversion recovery.

Some large molecules can bind water molecules for a time that is much longer than their native correlation time. This occurs at chemically conditioned sites in the inner coordination shell of such molecules in the presence of exchange with bulk water. These sites are termed the *inner sphere*. The increase in the correlation time results in an enhanced relaxation. Consider for example gadolinium chelates [4] which are currently the main type of contrast agent used in the clinical routine. The binding of water molecules contributes about the half of the relaxation effect in the case of Gd-ECF agent [5]. The other half is due to diffusion of water molecules in the magnetic field created by the paramagnetic Gd-ion. This mechanism is termed as taking place in the *outer sphere*. This is the only mechanism of relaxation enhancement by superparamagnetic particles of iron oxide [6, 7, 8], since the current coating of these particles does not have any coordination sites for water.

Doping water with paramagnetic particles increases the magnitude of random magnetic field experienced by nuclear spins in proportion to Ω^2 which causes the effect on relaxation to be significant for even low concentrations of such agents. The value Ω^2 is in turn proportional to the squared magnetic moment of molecules thus determining the same dependence of the outer-sphere relaxation rate [4].

2.5 Conclusion

The above discussion concerns the basic qualitative features of the longitudinal and transverse relaxation. We have used the *semiclassical* approach describing the spins in terms of quantum mechanics and the environment as the source of a classical random magnetic field. A more detailed *quantum* description engages quantum mechanics for both the spins and the environment. This leads to the same results for the relaxation rates as in the semiclassical approach. The actual outcome of the quantum description is the correct prediction of the equilibrium magnetization of nuclear spins. In the rest of this note, we sketch a way for quantitative analysis of relaxation using the semiclassical description.

3 Quantitative Description of Relaxation

3.1 Semi-Classical Description of Relaxation

Consider an individual spin interacting with its environment as with a thermal bath. This environment is conventionally called the *lattice* in the spirit of NMR in solids, even when one considers NMR in liquids. The presence of a large number of degrees of freedom in the lattice suggests that its behaviour can be described with a significant degree of averaging of all quantities to their classical values. We treat each spin individually as a quantum system subjected to a classical "force" which results from averaging of the degrees of freedom in the lattice.

The evolution of a spin is described by the Schrödinger equation

$$i\hbar \frac{d}{dt} \psi = H \psi , \quad (3)$$

where ψ is described by the spinor given in the first equality in Eq.(1) and H is the Hamiltonian. It consists of two terms, $H = H_0 + V$, that describe the free spin precession and the action of the lattice respectively.

The term H_0 is defined by the interaction of the main magnetic field, \vec{B}_0 , with the magnetic moment, $\vec{\mu}$, associated with the spin: $H_0 = -\vec{\mu} \cdot \vec{B}_0 = -\gamma \vec{S} \cdot \vec{B}_0 = -\hbar \omega_0 \sigma_z / 2$. We use here the convention that the third axis is selected parallel to the main field. \vec{S} is the operator of spin consisting of components S_a , $a = x, y, z$ and σ_z is the third of the Pauli matrices selected here in the following form:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} , \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} , \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} . \quad (4)$$

The perturbation term is a 2×2 matrix with the time-dependent components:

$$V = \begin{pmatrix} V_{11}(t) & V_{12}(t) \\ V_{21}(t) & V_{22}(t) \end{pmatrix} . \quad (5)$$

As any physical quantity, this matrix must be Hermitian, $V = V^\dagger$. The time dependence of the coefficient is random. It is convenient to rewrite the equation in the form $V = \hbar \Omega$, where Ω has the dimension of frequency rather than energy. Explicitly,

$$V = \hbar \begin{pmatrix} \Omega_{11}(t) & \Omega_{12}(t) \\ \Omega_{21}(t) & \Omega_{22}(t) \end{pmatrix} . \quad (6)$$

The Schrödinger equation takes now the form

$$i \frac{d}{dt} \begin{pmatrix} u \\ v \end{pmatrix} = \left[\begin{pmatrix} \omega_0/2 & 0 \\ 0 & -\omega_0/2 \end{pmatrix} + \begin{pmatrix} V_{11}(t) & V_{12}(t) \\ V_{21}(t) & V_{22}(t) \end{pmatrix} \right] \begin{pmatrix} u \\ v \end{pmatrix} , \quad (7)$$

This explicit form will be used in what follows along with the abbreviated notations introduced above.

Solving Eq. (7) simplifies substantially if we take into account a significant difference in the magnitudes of the two terms of the Hamiltonian. The magnitude of the Larmor frequency, ω_0 is typically of the order of 10^8 s^{-1} . The relaxation times are known to be of the order of 0.1 – 1 seconds in water which corresponds to the characteristic frequency of 1–10 Hz. This value is at least 10^7 times smaller than the Larmor frequency. We use this fact in order to find an approximate solution to Eq. (7) accounting only for the first nonvanishing correction in Ω/ω_0 . This approach termed *perturbation theory* belongs to the main methods of quantum mechanics. It is described below for the sake of completeness and adaptation of general rules to the specific case of spin 1/2.

3.2 Properties of the Perturbation

We undertake several steps toward the solution of Eq. (7) in order to analyse the effect of the random field V which we refer to as the perturbation. It is convenient to search for the solution in the form

$$\begin{pmatrix} u(t) \\ v(t) \end{pmatrix} = \begin{pmatrix} e^{i\omega_0 t/2} & 0 \\ 0 & e^{-i\omega_0 t/2} \end{pmatrix} \begin{pmatrix} p(t) \\ q(t) \end{pmatrix}. \quad (8)$$

This substitution is conventionally abbreviated as $\psi = e^{-iH_0 t/\hbar} \eta$, where η is the spinor with the components p and q . The exponential function or an arbitrary function f of the matrix should be understood with respect to the basis in which H_0 is diagonal. The matrix $f(H_0)$ is a diagonal matrix in which the eigenvalues of H_0 , λ_n are replaced with $f(\lambda_n)$ as in Eq. (8). The spinor η describes the spin in the reference frame that rotates with the Larmor frequency. Substitution of Eq. (8) in Eq. (7) results in

$$i \frac{d}{dt} \eta(t) = \tilde{V}(t) \eta(t), \quad (9)$$

where

$$\tilde{V} = e^{+iH_0 t/\hbar} V(t) e^{-iH_0 t/\hbar} \eta(t). \quad (10)$$

To obtain these equations, we have multiplied Eq. (8) by $e^{+iH_0 t/\hbar}$ from the left in order to isolate the time derivative of η . It follows from Eq. (9) that the pure Larmor precession ($V = 0$) is described by a constant spinor, $\eta = \eta_0$ as it should be in the rotating frame. The effect of perturbation is collected in the time dependence of $\eta(t)$.

It is reasonable to begin the analysis with the form of the perturbation in Eq. (9). A straightforward matrix multiplication yields

$$\tilde{V}(t) = \begin{pmatrix} V_{11}(t) & V_{12}(t) e^{-i\omega_0 t} \\ V_{12}^*(t) e^{+i\omega_0 t} & V_{22}(t) \end{pmatrix}. \quad (11)$$

As any Hermitian 2×2 matrix, $\tilde{V}(t)$ can be expanded in four basis matrices: unity matrix, $\mathbb{1}$, and the three Pauli matrices given in Eq. (4):

$$\tilde{V}(t) = V_0(t) \mathbb{1} + V_z(t) \sigma_z + V_+(t) \sigma_+ e^{i\omega_0 t} + V_-(t) \sigma_- e^{-i\omega_0 t}. \quad (12)$$

Here

$$V_0 = \frac{V_{11} + V_{22}}{2}, \quad V_z = \frac{V_{11} - V_{22}}{2}, \quad V_+ = V_{12}, \quad V_- = V_{21} = V_+^* \quad (13)$$

and matrices σ_{\pm} are the ladder operators for the spin:

$$\sigma_+ = \frac{\sigma_x + i\sigma_y}{2} = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad \text{and} \quad \sigma_- = \frac{\sigma_x - i\sigma_y}{2} = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}. \quad (14)$$

The above representation displays the action of different components of the perturbation on the spin which can be analyzed using Eq. (9) in the form

$$\frac{d}{dt}\eta(t) = -i\tilde{V}(t)\eta(t) . \quad (15)$$

This is an explicit expression for the time derivative of η at a given moment of time. We use it to find the spinor in the next moment: $\eta(t + \Delta t) = \eta(t) - i\Delta t\tilde{V}\eta(t)$. For $\Delta t \rightarrow 0$, each term in \tilde{V} contributes independently to the change in η . Thus we can analyse the trend in the time dependence of $\eta(t)$. For example, the term V_0 results in the following transform

$$u(t + \Delta t) = (1 - iV_0(t)\Delta t)u(t) \quad , \quad v(t + \Delta t) = (1 - iV_0(t)\Delta t)v(t) . \quad (16)$$

This does not imply any change in the relative phase between the upper and the lower components of the spinor that defines the angle φ in Eq. (1) which is the phase spin precession. Similarly, the term $V_z\sigma_z$ generates the following transform

$$u(t + \Delta t) = (1 - iV_z(t)\Delta t)u(t) \quad , \quad v(t + \Delta t) = (1 + iV_z(t)\Delta t)v(t) . \quad (17)$$

Due to the smallness of Δt , this can be represented as $u(t + \Delta t) = e^{-iV_z(t)\Delta t}u(t)$ and $v(t + \Delta t) = e^{iV_z(t)\Delta t}v(t)$. The infinitesimal change in the relative phase of the two spinor components is $2V_z(t)\Delta t$. Thus the term V_z contributes to the change in the precession phase. A phase dispersion in the sample arises due to this term which is thus the source of the transverse relaxation. This can be expected, since the term $V_z\sigma_z$ describes the action of a magnetic field parallel to \vec{B}_0 .

The longitudinal relaxation is described by V_+ and V_- which are coupled to the operators of the spin flip. These terms originate from the x and y components of the local magnetic field. The action of these operators is accompanied by multiplication with the exponential factor $e^{\pm\omega_0 t} = e^{\pm\Delta E t/\hbar}$, where ΔE is the energy difference between the two Zeeman levels of the spin.

3.3 Why Do We Need the Density Matrix?

Equation (9) can be solved perturbatively as an expansion $\eta = \eta_0 + \eta_1 + \eta_2 + \dots$ in which each term is proportional to the corresponding power of $\tilde{V}(t)$. This would give the spinor for a specific time course of the perturbation. A further operation would be to calculate the averaged spin according to the rules of quantum mechanics and only then average the result over all possible realizations of the random function $\tilde{V}(t)$. It is inconvenient to perform additional steps having already solved the main equation. This can be illustrated by a problem to describe the zero mean magnetization in the sample. A single spin has always a direction as follows from Eq. (1). The zero total magnetization is a result of incoherent addition of contributions of individual spins. This fact is obscured in the description based on individual spinor such as in Eq. (9).

The standard way to overcome this problem is to perform the averaging over the statistical ensemble *prior* to solving the Schrödinger equation. The solution is then formulated in terms of the *density matrix*, ρ which is bilinear in the original spinors. The derivation of the density matrix is given in many textbooks. A suitable reference in the present context is Ref. [1, chapter 4]. The average value of a physical quantity Q is given by

$$\langle Q \rangle = \text{Tr } \rho Q . \quad (18)$$

This operation includes both the quantum mechanical and the statistical averaging. The content of the density matrix can be clarified by calculating the mean values of all three components of the spin operator and expressing the elements of ρ in terms of these quantities. This yields

$$\rho = \begin{pmatrix} 1 + s_z & s_- \\ s_+ & 1 - s_z \end{pmatrix} , \quad (19)$$

where $s_{\pm} = s_x \pm is_y$ and s_x , s_y and s_z are the mean values of the three spin components. Note that these quantities are proportional to the macroscopic nuclear magnetization in the sample. In particular, s_+ determines the complex-valued signal acquired in MR scanners. The representation in Eq. (19) enables writing any given value of the mean spin, in particular $\vec{s} = 0$.

The Schrödinger equation, Eq. (9), takes the following form in terms of the density matrix

$$i \frac{d\rho}{dt} = [\tilde{V}, \rho] , \quad (20)$$

where $[\tilde{V}, \rho] = \tilde{V}\rho - \rho\tilde{V}$ is the commutator of two matrices. This equation is already written in the rotating frame.

3.4 Perturbative Solution for Density Matrix

We search for the solution to Eq. (20) in the form of a power series in \tilde{V} :

$$\rho = \rho_0 + \rho_1 + \rho_2 + \dots \quad (21)$$

Substitution of this expansion in Eq. (20) and equating terms of the same order in \tilde{V} gives the following recursive set of equations

$$\frac{d}{dt}\rho_0 = 0 \quad (22)$$

$$\frac{d}{dt}\rho_1 = -\frac{i}{\hbar}[\tilde{V}, \rho_0] \quad (23)$$

$$\frac{d}{dt}\rho_2 = -\frac{i}{\hbar}[\tilde{V}, \rho_1] \quad (24)$$

...

The solution is obtained by a straightforward integration which gives a constant ρ_0 and

$$\rho_1(t) = -\frac{i}{\hbar} \int_0^t dt_1 [\tilde{V}(t_1), \rho_0] \quad (25)$$

$$\rho_2(t) = -\frac{1}{\hbar^2} \int_0^t dt_2 dt_1 [\tilde{V}(t_2), [\tilde{V}(t_1), \rho_0]] . \quad (26)$$

Let us discuss each of these three terms.

The constant value of ρ_0 corresponds to the fact that the mean nuclear magnetization remains constant in the rotating frame in the absence of interaction. A correction comes from the first-order term, Eq. (25). However, this correction does not affect the constant mean value of magnetization, as the time integral in Eq. (25) varies randomly around zero according to the stochastic character of $\tilde{V}(t)$. This does not result in any systematic drift in the density matrix.

Such a systematic change appears in the second order, Eq. (26). To see that, we analyse the time dependence of $\tilde{V}(t)$ which is due to the random variations of $V(t)$ and to the exponential factors in Eq. (10). It is convenient to represent the decomposition in Eq. (12) in the following form

$$\tilde{V}(t) = \sum_{\alpha} V_{\alpha}(t) \sigma_{\alpha} e^{i\omega_{\alpha}t} = \sum_{\alpha} V_{\alpha}(t)^* \sigma_{\alpha}^{\dagger} e^{-i\omega_{\alpha}t} . \quad (27)$$

The double form of this operator expresses the fact that it is Hermitian. The summation index takes the values $\alpha = z, +, -$ in agreement with Eq. (12). The values of ω_{α} are different for different α . The term

proportional to the unitary matrix is omitted, since it commutes with any ρ_0 . A substitution of $\tilde{V}(t_2)$ and $\tilde{V}(t_1)$ with the middle and the last expressions in Eq. (27) respectively results in the following form of ρ_2

$$\rho_2(t) = -\frac{1}{\hbar^2} \sum_{\alpha\beta} [\sigma_\alpha, [\sigma_\beta^\dagger, \rho_0]] \int_0^t dt_2 \int_0^{t_2} dt_1 V_\alpha(t_2) V_\beta(t_1)^* e^{i\omega_\alpha t_2 - i\omega_\beta t_1} . \quad (28)$$

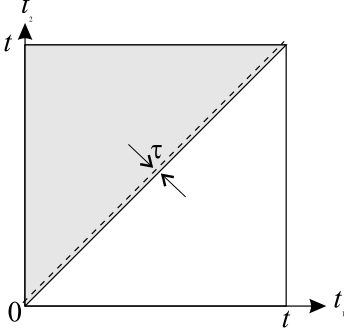


Fig. 5

The integration area in the (t_1, t_2) -plane is shown in figure 5 with the gray triangle. The value of the time t should be small as compared with the relaxation time, for example it can be selected in the submillisecond range. This time is still much longer than the correlation time. A systematic drift in the density matrix is present if the integral in Eq. (28) is proportional to this large time. This is the case for the terms in the double sum for which $\alpha = \beta$. In this case the integrand does not oscillate in the direction parallel to the diagonal of the square shown in figure 5. All other terms are small due to the fast oscillations in the whole integration area. The neglect of such terms casts the second-order contribution in the form

$$\rho_2(t) = -\frac{1}{\hbar^2} \sum_{\alpha} [\sigma_\alpha, [\sigma_\alpha^\dagger, \rho_0]] \int_0^\infty d\Delta t \int_0^t dt_1 V_\alpha(t_1 + \Delta t) V_\alpha(t_1)^* e^{i\omega_\alpha \Delta t} , \quad (29)$$

where the new variable is $\Delta t = t_2 - t_1$. The main contribution to the original integral comes from the region in which $t_2 - t_1$ is of the order of τ and the random functions $V_\alpha(t_2)$ and $V_\beta(t_1)$ are correlated. This region is represented in figure 5 as the area between the dashed line and the diagonal of the square. By this reason, the integration over Δt in Eq. (29) is extended to infinity.

The integration over t_1 in Eq. (29) performs the averaging of the product $V_\alpha(t_1 + \Delta t) V_\alpha(t_1)^*$, since the range of integration from zero to t is very large. We assume that the random function $V_\alpha(t)$ takes all possible values during this time. This means that we can replace the product with its averaged value:

$$\int_0^t dt_1 V_\alpha(t_1 + \Delta t) V_\alpha(t_1)^* \equiv t G_{\alpha\alpha}(\Delta t) , \quad (30)$$

where $G_{\alpha\alpha}$ is by definition the autocorrelation function of V_α . The remaining integration fulfills the Fourier transformation of $G_{\alpha\alpha}$:

$$\int_0^\infty d\Delta t G_{\alpha\alpha}(\Delta t) e^{i\omega_\alpha \Delta t} = J_{\alpha\alpha}(\omega_\alpha) . \quad (31)$$

This quantity is the spectral density of perturbation involved in the discussed in section 2.3 above.

The final result for ρ_2 takes the form

$$\rho_2(t) = -\frac{t}{\hbar^2} \sum_{\alpha} [\sigma_\alpha, [\sigma_\alpha^\dagger, \rho_0]] J_{\alpha\alpha}(\omega_\alpha) . \quad (32)$$

This formula shows that ρ_2 brings a small correction, which is linear in time, to ρ_0 . This change in the density matrix is effective on a coarse-grained time scale. The value of t should be shorter than the observed relaxation time, but it is much longer than the typical time of microscopic processes set by the correlation time τ . This means that Eq. (32) expresses the time derivative of ρ on the macroscopic time scale. We rewrite this formula in terms of the total density matrix:

$$\frac{d}{dt}\rho(t) = -\frac{1}{\hbar^2} \sum_{\alpha} [\sigma_{\alpha}, [\sigma_{\alpha}, \rho]] J_{\alpha\alpha}(\omega_{\alpha}) . \quad (33)$$

Using the explicit expression given in Eq. (12), this formula takes the form

$$\frac{d}{dt}\rho(t) = -\frac{1}{\hbar^2} ([\sigma_z, [\sigma_z, \rho]] J_{zz}(0) + [\sigma_+, [\sigma_-, \rho]] J_{+-}(\omega_0) + [\sigma_-, [\sigma_+, \rho]] J_{-+}(\omega_0)) , \quad (34)$$

where $J_{-+}(\omega_0) = J_{+-}(\omega_0)^*$.

Consider now an arbitrary magnetization described by the density matrix given in Eq. (19). We substitute it in Eq. (34) and find the change in the magnetization. The double commutators can be calculated straightforwardly, but it is more convenient to decompose the density matrix as

$$\rho = \mathbb{1} + s_z \sigma_3 + s_+ \sigma_+ + s_- \sigma_- \quad (35)$$

and to use the following commutation relations

$$[\sigma_3, \sigma_+] = 2\sigma_+ , \quad [\sigma_3, \sigma_-] = -2\sigma_- , \quad [\sigma_+, \sigma_-] = \sigma_3 . \quad (36)$$

Equations for the component of the density matrix are obtained by equating the coefficient in front of the Pauli matrices on both sides of Eq. (34). This results in

$$\frac{ds_z}{dt} = -\frac{2}{\hbar^2} (J_{+-}(\omega_0) + J_{-+}(\omega_0)) s_z , \quad (37)$$

$$\frac{ds_+}{dt} = -\frac{2}{\hbar^2} (2J_{zz}(0) + J_{+-}(\omega_0)) s_+ . \quad (38)$$

These equations describe the monoexponential relaxation with the rates

$$R_1 = -\frac{2}{\hbar^2} (J_{+-}(\omega_0) + J_{-+}(\omega_0)) , \quad (39)$$

$$R_2 = -\frac{2}{\hbar^2} (2J_{zz}(0) + J_{+-}(\omega_0)) . \quad (40)$$

$$(41)$$

The results obtained are further applied to specific mechanisms of relaxation which define the form of the functions J_{zz} and J_{+-} . In particular, the number of quantum states under consideration should be increased to from two to four to describe the relaxation rate caused by the dipole - dipole interaction of spins in the same molecule either identical [9] or different [10, 11]. We stop at this point and address the reader to the literature.

3.5 Semiclassical Approach vs Quantum Theory

The most adequate theory of relaxation involves quantum mechanics to describe both the spin system and the lattice. This does not change the final expression for the relaxation rates obtained semiclassically, Eqs. (39) and (40) [12, chapter 8]. The quantum theory complements the semiclassical approach by specifying the equilibrium state toward which the spins relax. In the semiclassical theory, the longitudinal magnetization vanishes in the equilibrium state ($s_z = 0$ is the stationary solution to Eq. (37)). In reality, the equilibrium magnetization is defined by the Boltzmann distribution,

$$\rho_{eq} = e^{-H_0/kT} = \begin{pmatrix} e^{-\hbar\omega_0/2kT} & 0 \\ 0 & e^{+\hbar\omega_0/2kT} \end{pmatrix} \approx \begin{pmatrix} 1 - \frac{\hbar\omega_0}{2kT} & 0 \\ 0 & 1 + \frac{\hbar\omega_0}{2kT} \end{pmatrix}, \quad (42)$$

where we take into account that the Zeeman energy is much smaller than kT in the liquid state.

The quantum theory shows how the Boltzmann distribution in the spin system is induced by the same distribution in the lattice. The thermal equilibrium of the lattice is not affected by perturbations of the spin subsystem, since the latter has much less degrees of freedom than in the whole thermal bath. Details and further references are available in the literature [12, 1], see also [13].

The quantum theory of relaxation results in a substitution of the density matrix in Eqs. (33) and (34) with its deviation from the equilibrium: $\rho \rightarrow \rho - \rho_{eq}$. This is the only change in the above calculations which lead to $s_z \approx -\hbar^2\omega_0/2kT$ in the equilibrium.

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